

## A BAYESIAN TEMPERATURE DEPENDENT FLUCTUATION EXPRESSION IN CANONICAL ENSEMBLES

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### ABSTRACT

In this work, a new model for fluctuations in Canonical ensembles for which the partition function  $Q$  is independent on the number of molecules, ( $N$ ), the volume component ( $V$ ), and temperature (in the form of  $\beta=(kT)^{-1}$ , where  $T$ =temperature,  $k$ =Boltzman's constant). Our model incorporates the basic form of Baye's theorem, and will be applied to a real example for which the probability of the expected value of the energy given the temperature will be calculated. In essence an expression for the thermal energy in these fluctuations is presented.

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### INTRODUCTION

The basic methods of Statistical Mechanics<sup>1-4</sup> allow for use to calculate ensemble averages of mechanical variables, which are used to calculate adequate thermodynamic functions. The second central moment  $\overline{(X-\bar{X})^2}$  is a measure of the probability distribution about a mean value. Any deviation of any mechanical variable (not necessarily mechanical, used for purposes of an example) from the mean value is defined as a fluctuation, and thus our investigations of the probability of these fluctuations are then called theories of fluctuation. We will need to determine as to what extent we expect to see these fluctuations from the mean value. If the spread is in fact large, we could observe a range of values. Many theories of light scattering, and liquids depend on fluctuation theory, and thus are of importance to mathematicians, theoretical chemists/physicists, and a great body of experimentalists.

In this work we consider a canonical ensemble, were  $N$ ,  $V$  are constant. However, the effects of the most probable energy given with a known temperature interval can be calculated from a Bayesian analysis of the ensembles.<sup>5-6</sup> The most significant

application of this work lies in the determination of the lowest vibrational energy states of molecular complexes or species. If we can sum over all probable energies under a predicted vibrational energy, then a more accurate description of the zero-point energy effects can be evaluated, quite easily.

### MATHEMATICAL MODEL

By the basic equations for the variance of the energy in a fluctuation,<sup>1-4</sup> we get the following equation:

$$\sigma^2_E = \overline{(E - \bar{E})^2} = \overline{E^2} - \bar{E}^2 = \sum_j E_j^2 P_j - \bar{E}^2 \quad (1)$$

From this equation, E is the energy, and P<sub>j</sub> is the probability of a system being in the j<sup>th</sup> energy state with energy E<sub>j</sub>:

$$P_j = \frac{\exp[-\beta E_j]}{Q(N, V, \beta)} \quad (2)$$

In equation (2), the terms are defined in the same way as equation (1) with  $\beta = (kT)^{-1}$  (T=temperature, k is the Boltzmann constant or  $1.379 \times 10^{23}$  L atm K<sup>-1</sup>), and Q being the basic partition function for an N, V, T system, with the general form of Q (N, V,  $\beta$ ) =  $\sum \Omega(N, V, E) e^{-E\beta}$ , where  $\Omega(N, V, E)$  is the micro-canonical ensemble function. By using expression (1) and squaring the energy we get the following equation:

$$\sum_j E_j^2 P_j = \frac{1}{Q} \sum_j E_j^2 \exp[-\beta E_j], \quad (3)$$

leading to:

$$-\frac{1}{Q} \frac{\partial}{\partial \beta} \sum_j E_j^2 \exp[-\beta E_j] = -\frac{1}{Q} \frac{\partial}{\partial \beta} (\bar{E} Q) = -\frac{\partial \bar{E}}{\partial \beta} - \bar{E} \frac{\partial \ln Q}{\partial \beta}, \quad (4)$$

and finally:

$$\sum_j E_j^2 P_j = kT^2 \frac{\partial \bar{E}}{\partial T} + \bar{E}^2 \quad (5)$$

The variance can be expressed as,<sup>4</sup> where the heat capacity is defined as C<sub>v</sub> (for an ideal gas, C<sub>v</sub>=(3/2) NK):

$$\sigma_E^2 = kT^2 \left( \frac{\partial \bar{E}}{\partial T} \right)_{N,V} = kT^2 C_v, \quad (6)$$

and:

$$\sigma_E / \bar{E} = \frac{(kT^2 C_v)^{1/2}}{\bar{E}}. \quad (7)$$

An expression for the probability at constant temperature is given as:

$$P(E) = P\{\bar{E}\} \exp \left[ \frac{-(E - \bar{E})^2}{2kT^2 C_v} \right]. \quad (8)$$

However, in equation (8) the temperature is assumed to be constant, and that it does not change under changing conditions. In this regard, we applied the Bayesian model (general form:  $P(X|Y) = P(X)P(Y)/(P(X)+P(Y))$ )<sup>5-6</sup> to get the expected value of the energy ( $E$ ), at a given temperature (i.e. the lowest vibrational states of a molecular complex):

$$P(E|T) = P\{\bar{E}\}P(T) \exp \left[ \frac{-(E - \bar{E})^2}{2kT^2 C_v} \right], \quad (9)$$

for an ideal gas:

$$P\{\bar{E}\} \rightarrow 2\pi kT^2 C_v. \quad (10)$$

From our Bayesian treatment (and integration over all space):

$$P(E|T) = \int \frac{P(E)^2 P(T)}{P(E) + P(T)} \exp \left[ \frac{-(E - \bar{E})^2}{2kT^2 C_v} \right] dT, \quad (11)$$

where (for an ideal gas under our model) [1]:

$$P(E) \rightarrow N^{-1/2}, \quad \bar{E} = \frac{3kT}{2}. \quad (12)$$

In the above expressions,  $N$ =number of molecules per mole (for an ideal gas it is defined as  $6.022 \times 10^{23}$  atoms, molecules or particles per mole).

### NUMERICAL EXAMPLE

In an application of this newly derived Bayesian model, we consider a case where the energy of a complex or molecule differs from the average energy for one mole of an ideal gas, under standard conditions, by  $10^{-4}$  percent (equation (E1)):

$$(E - \bar{E}) = 10^{-4} \bar{E}. \quad (\text{E1})$$

Thus, the probability of observing this energy state is given as:

$$P(E | T) = \int_0^{\infty} \frac{N^{-1} P(T)}{N^{-1/2} + P(T)} \exp\left[\frac{-10^{-8} (3/2)^2 k^2}{2k(3/2)NK}\right] dT, \quad (\text{E2})$$

which can be summed over all space. In this example we have integrated for all temperatures from 0 to 10 (reduced temperature units, or kT units), since N is large:

$$P(E | T) = \exp\left[\frac{-10^{-8} (3/2)^2 k^2}{2k(3/2)NK}\right] \sum_{P(T)=0}^{10} \frac{N^{-1} P(T)}{N^{-1/2} + P(T)}, \quad (\text{E3a})$$

with our numerical Monte Carlo simulation performed with the following step size:

$$\Delta P(T) = 0.01. \quad (\text{E3b})$$

The Monte Carlo simulations were performed with a very small step size, in order to ensure that a very accurate result for the probabilities can be obtained. Since N is very large,  $P(E|T) \rightarrow 0$ , as  $P(T) \rightarrow \infty$ . The simulations were run on UNIX, LINUX, WIN NT, WIN 98, WIN XP, and AIX in order to insure consistency in the computational results.

This gives a final result of:

$$\begin{aligned} P(E | T) &= 1.6605 \times 10^{-23} \\ P(E | T) / \text{mole} &= 10.000 \end{aligned} \quad (\text{E4})$$

The final result in (E4) was obtained by multiplying the result by Avogadro's number ( $=6.022 \times 10^{23}$  atoms, molecules or particles per mole). The reason we chose (for this example), all temperatures from 0 to 10 K is because this is the typical range by which experimentalists deal with to suppress any zero-point effects.

### CONCLUSIONS

Our presented method allows for a more accurate calculation of the probability of observing a particular energy state (in a state of fluctuation), by just having a changing

temperature. In most results presented to date, multiple data points need to be known before this probability is obtained, without an account of temperature changes. The relative difference of the energy from the average value of the energy in a system (under an ideal gas state) in equation E (1), as well as the probability under a different temperature (T) interval defined by E (3) can be modified to fit any given set of conditions, and thus the lowest vibrational state determined. In any case the result in E (4) is the value of the reduced energy (unit less values described elsewhere in statistical problems) per mole of atoms, molecules or particles. We have thus presented an expression for the most probably energy state (under low temperature conditions) as a function of temperature, in other words the thermal energy for fluctuations in canonical ensembles (for an ideal gas) is calculated by Monte Carlo methods. These methods are extremely useful to Molecular Dynamics simulations since they allow for a computation of the possible fluctuations by simply taking into account temperature changes, and these fluctuations (of the temperature and/or energy) critically depend on the size of the system and coupling (functional form plus the strength) to the external thermal bath. Unlike previous models, that deal with the quasi-Gaussian entropy theory,<sup>5-6</sup> which allow for the calculation of the Helmholtz free energy based on the potential energy distribution function our model allows for the computation of thermodynamic relationships from changes (or fluctuations) in temperature alone in canonical ensembles. We are currently in the process of extending our models to include wide ranges of properties and functions in different ensembles.<sup>7</sup>

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#### REFERENCES

1. D. McQuarrier, *Statistical Mechanics*, 2000, University Science Books, New York, Chapter 3.
2. N. Davidon, *Statistical Mechanics*, 1962, Mc-Graw Hill, New York, Chapter 12-14.
3. J. Kestin, J. R. Dorfman, *Statistical Thermodynamics*, 1971, Academic Press, New York, Chapter 14.
4. L. D. Landau, E. M. Lifshitz, *Statistical Physics*, 1958, London, Pergamon Press, Chapter 12.
5. A. Amadei, M. E. F. Apol, A. Di Nola and H. J. C. Berendsen, *J. Chem. Phys.* 1996,104, 1560-1574.
6. M. E. F. Apol, A. Amadei and H. J. C. Berendsen, *J. Chem. Phys.* 1996,104, 6665-6678.

7. A. F. Jalbout (work in progress).

### **Povzetek**

Predstavljamo nov model fluktuacij v kanonskih setih, ki vključuje Baye-ev teorem. Model smo preverili na realnem primeru, pri katerem smo izračunali temperature za pričakovano vrednost energije. CV bistvu predstavljamo izraz za termično energijo fluktuacij v kanonskih setih.